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Published on 03 July 2012 on http://pubs.rsc.org | doi:10.1039/C2CC34176J

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ARTICLE TYPE

EVALUATE: Highly π electron-rich macro-aromatics. Bis(*p*-aminophenyl)-*carbo*-benzenes and their DBA acyclic references#

Arnaud Rives,^{a,b} Iaroslav Baglai,^{a,b,c} Volodymyr Malytskyi,^{a,b,c} Valérie Maraval,^{*a,b} ⁵ Nathalie Saffon-Merceron,^b Zoia Voitenko^c and Remi Chauvin^{*a,b}

Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX DOI: 10.1039/b000000x

A series of stable quadrupolar bis(p-aminophenyl)-carbobenzenes, featuring both donor-donor-donor π -frustration and 10 central macro-aromaticity, is described and compared to the acyclic dibutatrienylacetylene (DBA) reference series.

4,4"-Diamino-p-terphenyl (DATP) is a valuable motif for the design of electroluminescent devices.¹ From the fundamental viewpoint, the π -donating character of the two nitrogen atoms 15 flanking the π -electron-rich terphenyl rod makes it an *a priori* " π -frustrated" motif,² which ground state is stabilized by *local* aromaticity of π -independent phenylene rings, while low lying excited states may acquire global aromaticity in a coplanar geometry.³ The invoked aromaticity can be quantified by 20 aromatic stabilization energies (ASEs) between the π -cyclic structure and acyclic reference components (Fig. 1).^{4,5} While many ASEs have been theoretically devised, their generality vs the substitution pattern and their experimental realization have been scarcely addressed in an explicit manner.⁵ A 25 chemically relevant simple definition for the range of quadrupolar benzene derivatives relies on an eliminative [4+2] retro-Diels-Alder process, where the C₄ moiety preserves a π -

conjugation between electro-active ends. For DATPs, the C₄ components are di(*p*-aminophenyl)butadienes (DAPBs), that $_{30}$ have long been used as key chromophoric units as well.⁶



Fig. 1 Simple *carbo*-meric ASE equations for the central ring of quadrupolar terphenyl derivatives (DATPs) and *carbo*-mers thereof.

The relevance of ASE definitions is also submitted to the ³⁵ condition that their absolute value should vanish, or at least decrease, with the ring size.⁴ A ring-expanded version of DATP is its central ring *carbo*-mer,⁷ i.e. bis(*p*-aminophenyl)*carbo*-benzene (*carbo*-DATP). Although most of the known *carbo*-benzenes are aryl-subtituted (derivatives of **1a**, Fig. 1),⁷ ⁴⁰ the aromaticity of the C₁₈ ring has been long regarded as a key stabilization factor.⁸ Recently, however, π-acyclic dibutatrienylacetylene (DBA) sub-motifs (*carbo*-mers of butadiene) were also found to be quite stable.⁹ This allows the "macroaromaticity" of *carbo*-DATPs to be addressed by comparison ⁴⁵ to their DBA-type components, here denoted as *carbo*-DAPBs. "Macro-aromaticity" is indeed commonly invoked for porphyrins,¹⁰ in which frontier electronic excitations exhibit strong analogy with those of *carbo*-benzenes:¹¹ this was illustrated for the dianisyl derivative **1b**, a moderately "π-⁵⁰ frustrated"² parent of the di(aminophenyl) series disclosed below, and consisting in two sub-series: the anilinyl type, and the indolylphenyl type (Scheme 1).



Scheme 1 Synthesis of carbo-DATPs.

⁵⁵ Macrocyclic *carbo*-DATPs were prepared from the known [6]pericyclynedione 2,^{11,12} which was reacted with anilinyl Grignard reagents (4-NR₂-C₆H₄MgBr, R = TMS, Me) to give the acid-sensitive [6]pericyclynediols 3a and 3b as crude materials only. The more stable indolyl and carbazolyl ⁶⁰ derivatives 4 and 5, respectively generated from Grignard and lithium reagents, were purified as mixtures of stereoisomers.¹³ The [6]pericyclynediols 3-5 were then treated with SnCl₂/HCl

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in either DCM or Et₂O, ^{9h} followed by aq. NaOH (Scheme 1). Crude samples of **3a** and **3b** were thus converted to the acidsensitive *carbo*-DATPs **6** (after concommitant N-desilylation) and **7**, in 26 % and 6 % yield from **2**, respectively, while pure 5 **4** and **5** afforded the stable *carbo*-DATPs **8** and **9** in *ca* 70 % yield. Both **7** and **9** proved poorly soluble, and full ¹³C NMR analysis of **9** required CP-MAS techniques. All the *carbo*-DATPs **6**-**9** are highly crystalline materials, but only crystals of **6** were found suitable for X-ray diffraction (XRD) analysis ¹⁰ (Fig. 2). In spite of a disorder between phenyl and anilinyl

substituents, quite accurate data were obtained in the classical range for the C_{18} macrocycle.^{8a-b,11} In solution, the macroaromaticity of **6-9** was confirmed by the deshielding of the *ortho-*¹H nuclei of the aryl rings in the range 9.2-9.6 ppm.



Fig. 2 Molecular views of the *carbo*-DATP 6 (*left*) and *carbo*-DAPB 17 (*right*. For 18, see Fig. S1 in the SI).

The *carbo*-DAPB acyclic counterparts of **6-9** (Fig. 1) were targeted from the triynedial **10**,¹² *via* the pentaynediol **11** and ²⁰ pentaynedione **12**, which reacted with selected Grignard or lithium reagents to give the diols **13-16** (Scheme 2). As in the cyclic series, while the acid-sensitive anilinyl derivatives **13** and **14** could not be purified, the indolylphenyl counterparts **15** and **16** were isolated in good yields.



Scheme 2 Four-step synthesis of the *carbo*-DAPBs 17-20. Treatment of 13-16 with SnCl₂/HCl, followed by aq. NaOH, was optimized from insights gained in the *carbo*-DATP series. Reaction of crude 13 in DCM thus afforded the N-desilylated 20 *carbo*-DAPB 17 as a dark-blue material in 53 % yield from

- 12. Reduction of 14, 16 to 18, 20 was found more efficient in Et_2O (29-52 % yields), while reduction of 15 to 19 was optimized to a 74 % yield in DCM over a short reaction time. Whereas NMR spectroscopy indicated that 17-20 occured as
- ³⁵ mixtures of isomers, XRD analysis of crystals of 17 (Fig. 2) and 18 (Fig. S1 in the SI) showed the all-*trans* isomers only.

Absorption spectra of the carbo-DATPs 6-9 and carbo-DAPBs 17-20 are shown in Fig. 3. The influence of the aminophenyl substituents on the λ_{max} value is similar in both 40 series, the higher bathochromic shift occuring for the dimethylaniline derivatives 7 and 18. The intrinsic aromaticity of the indolyl substituents makes them more innocent toward the central core (8-9 and 19-20 giving the same lowest λ_{max} values of 486.5±0.5 and 598±1 nm in each series), and the 45 more donating the substituent, the stronger the bathochromic shift. The range of variation of λ_{max} is twice as wide in the carbo-DAPB series ($\Delta \lambda_{max} = 72$ nm for 18-20) as in the *carbo*-DATP series ($\Delta \lambda_{max} = 35$ nm for 7-8). The λ_{max} values are also higher for carbo-DAPBs than for carbo-DATPs (by at 50 least 113 nm, for 8 and 19). These observations are consistent with the aromatic character of the carbo-benzene core, which should thus be more "insulating" than the more substituentsensitive acyclic DBA core. Although no rationale is obvious, the bathochomic effect of the donating character is found 55 prolounged beyond the aminophenyl series to the anisyl and phenyl substituents ($\lambda_{max}(\mathbf{1b}) = 482 \text{ nm} > \lambda_{max}(\mathbf{1a}) = 472$ nm).8a,11 As observed for other carbo-benzenes, the carbo-DATPs also exhibit a secondary band at higher wavelength (with relative intensity $7 > 6 > 8 \approx 9$), close to the λ_{max} value 60 of their DBA homologue in the range 600-650 nm.



Fig. 3 UV-vis spectra (in CHCl₃) of the *carbo*-DATPs **6-9** (*left*) and corresponding *carbo*-DAPBs **17-20** (*right*).

Emission spectra of **8-9** and **19-20** were compared to those of ⁶⁵ the respective diol precursors **4-5** and **15-16** serving as standards of the π -isolated fluorophoric units ($\lambda_{\rm Em} \approx 330$ nm for phenylindole, ¹⁴ $\lambda_{\rm Em} \approx 340$, 360 nm for phenylcarbazole).¹⁵ For the *carbo*-DATPs **8-9**, the wavelengths are similar in both absorption (486.5±0.5 nm) and emission (596±1 nm), and ⁷⁰ markedly different from those of **4-5**, in accordance with the increase of the conjugation extent and with previous results on N-arylcarbazole conjugates.¹⁶ The fluorescence intensity of **8-9** is also much lower than that of **4-5**, as expected from the reciprocal increase of the absorbance intensity. The same ⁷⁵ trends were observed for the *carbo*-DAPBs **19-20** vs **15-16**.

Table 1 Absorption (λ_{maxAbs}) and emission (λ_{Em} , vs λ_{exc}) wavelengths of *p*-N-indolyl- and *p*-N-carbazolyl-phenyl-substituted chromophores.^{*a,b*}



^{*a*} In CHCl₃ solutions, in nm units. Secondary bands are given in brackets. ^{*b*} λ_{Em} values do not vary upon shifting the λ_{exc} values to the λ_{maxAbs} values.

⁸⁰ Noteworthy, the $\lambda_{\rm Em}$ values of **19-20** (500±1 nm) are lower

than the λ_{maxAbs} values, with formal anti-Stokes shifts of – 98±2 nm, thus confirming that the fluorescence of **19-20** arises from electronic transitions corresponding to secondary bands of the absorption spectra, vibronically independent s from the DBA core-centered allowed main transition.^{9c,11}

- Electrochemical properties were finally investigated by square-wave (SWV) and cyclic (CV) voltammetry (Table 2). Similar reduction behaviors were observed in both series, with two reversible waves (except for 7 and, perhaps, 9), possibly
- ¹⁰ accompanied with an irreversible one. The first potential varies over a broader range in the *carbo*-DAPB series (from 0.75 V for **20** to -0.95 V for **18**) than in the *carbo*-DATP series (from -0.71 V for **8** to -0.85 V for **7**), thus confirming that the DBA core is more sensitive to substituent effects than
- ¹⁵ the *carbo*-benzene core. The indole derivatives (8-9, 19-20) are more readily reduced than the aniline analogues (6, 17), and still more than the dimethylaniline derivatives (7, 18). This is consistent with the relative π -donating character of the substituents. While indolyl substituents appear slightly less
- ²⁰ electron-donating than OMe substituents $(E_{1/2}(\mathbf{1b}) = 0.77 \text{ V})$,¹¹ the limit of reducibility (even at scan rate of 10 V.s⁻¹) is reached for the most π -frustrated *carbo*-DATP **7**.

In the oxidation regime, the cations of the less π -frustrated *carbo*-DATPs **6** ($E_p = 0.576$ V), **8** ($E_p = 1.050$ V) and **9** ($E_p =$

- ²⁵ 1.416 V), were found to deposit on the electrode, as observed for **1b** which value ($E_p = 0.90$ V) confirms the intermediate donating character of anisyl substituents *vs* anilinyl and indolylphenyl substituents.¹¹ The dimethylanilinyl homologue **7** is the most π -frustrated *carbo*-benzene reported to date, and
- ³⁰ undergoes a reversible oxidation at 0.512 V. Finally, the first oxidation potentials of the *carbo*-DAPBs **17-18** and **20** are reversible and close to those of their *carbo*-DATP parents.[‡]

Table 2 CV and SWV data for carbo-DATPs and carbo-DAPBs.^a



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^a Measurements at r.t. in DCM, 0.1 M [*n*-Bu₄N][PF₆]; electrodes: Pt
³⁵ (working), SCE (reference); scan rate: 0.2 V.s⁻¹ unless otherwise noted. ^b
0.1 V.s⁻¹. ^c Observed at 10 V.s⁻¹. ^d Undetermined reversibility due to the poor solubility of **9**. ^e The oxidation product deposited on the electrode.

Two series of " π -frustrated" *carbo*-benzenes and DBA acyclic references have been compared.² The relative stability of the

⁴⁰ latter illustrates a secondary effect of the macro-aromaticity of the former. Beyond the fundamental aspects, the "*carbo*-mer principle"⁷ now calls for the study of their electro-optical properties by comparison to their DATP and DAPB parents.

Notes and references

- 45 a CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, F-31077 Toulouse Cedex 4, France. Fax: +33 (0)5 61 55 30 03; Tel: +33 (0)5 61 33 31 13; E-mail: vmaraval@lcctoulouse.fr, chauvin@lcc-toulouse.fr b Université de Toulouse, UPS, ICT-FR2599, F-31077 Toulouse, France.
- 50 C Kiev National Taras Shevchenko University, 60 Volodymlyrska St, 01033 Kiev, Ukraine.

† Electronic Supplementary Information (ESI) available: experimental procedures, characterization and crystallographic details. CCDC 886379
(6), 886380 (17), 886381 (18). See DOI: 10.1039/b000000x/

- 55 ‡ The first oxidation waves of 17 and 18 are very intense, suggesting an overlap of two one-electron processes at the remote anilinyl motifs. This could not be confirmed by electrolysis because of product decomposition. #This article is part of the ChemComm 'Aromaticity' web themed issue.
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